CARBON ISOTOPES OF ALKANES IN HYDROTHERMAL ABIOTIC ORGANIC SYNTHESIS PROCESSES AT HIGH TEMPERATURES AND PRESSURES: AN EXPERIMENTAL STUDY. Qi Fu[1], Richard A. Socki[2], and Paul B. Niles[3], [1]Lunar and Planetary Institute, Houston, TX 77058 (fu@lpi.usra.edu), [2]ESCG, [3]KR, Astromaterials Research and Exploration Science, NASA Johnson Space Center, Houston, TX 77058.

Introduction: Observation of methane in the Martian atmosphere has been reported by different detection techniques [1-4]. With more evidence showing extensive water-rock interaction in Martian history [5-7], abiotic formation by Fischer-Tropsch Type (FTT) synthesis during serpentization reactions may be one possible process responsible for methane generation on Mars [8, 9]. While the experimental studies performed to date leave little doubt that chemical reactions exist for the abiotic synthesis of organic compounds by mineral surface-catalyzed reactions [10-12], little is known about the reaction pathways by which CO_2 and/or CO are reduced under hydrothermal conditions.

Carbon and hydrogen isotope measurements of alkanes have been used as an effective tool to constrain the origin and reaction pathways of hydrocarbon formation. Alkanes generated by thermal breakdown of high molecular weight organic compounds have carbon and hydrogen isotopic signatures completely distinct from those formed abiotically [13-15]. Recent experimental studies, however, showed that different abiogenic hydrocarbon formation processes (e.g., polymerization vs. depolymerization) may have different carbon and hydrogen isotopic patterns [16]. Results from previous experiments studying decomposition of higher molecular weight organic compounds (lignite) also suggested that pressure could be a crucial factor affecting fractionation of carbon isotopes [17]. Under high pressure conditions, no experimental data are available describing fractionation of carbon isotope during mineral catalyzed FTT synthesis. Thus, hydrothermal experiments present an excellent opportunity to provide the requisite carbon isotope data. Such data can also be used to identify reaction pathways of abiotic organic synthesis under experimental conditions.

Experiments: An experiment involving hydrothermal abiotic organic synthesis was performed using piston cylinder apparatus in the Multi-Anvil and High Pressure Lab at NASA Johnson Space Center (Fig. 1). A gold capsule (2 mm O.D. × 10 mm L) was used owing to its deformability and adequately chemical inertness under experimental conditions. Magnetite, the potential mineral catalyst, was synthesized from inorganic compounds following the method described in Schwertmann and Cornell (1991) [18], and was characterized by X-ray diffraction. Formic acid (HCOOH) was the source of dissolved H_2 and CO_2 in the experiment due to its decarboxylation at high temperatures. The Au capsule was loaded with 50 µL DI water, 2 µL formic acid, and magnetite before it was put in piston cylinder assembly.

The experiment was conducted at 750 ^oC and 0.55 GPa (1 GPa = 10 kb) for 4 hours. After isobaric quench with a quench rate of > 50 $^oC/s$, the Au capsule was recovered, and its outer wall was cleaned with acid. The volatile products were retrieved by puncturing the capsule in an evacuated container. The chemical and carbon isotope compositions of dissolved carbon species were determined by GC-C-MS-IRMS.

Results: To evaluate carbon background on magnetite surfaces and in the whole system, a control experiment was performed at the same T and P conditions with no formic acid present. No carbon-bearing compounds were detected by GC-MS, indicating the effectiveness of precluding other carbon sources than formic acid by this experimental approach.

Chemical compositions. For carbon-bearing compounds, dissolved CO_2, CH_4, and C_2H_6 were identified. Dissolved CO_2 was the dominant carbon species with its relative abundance of 88 mol%. Among alkanes, the mole abundance ratio of CH_4 and C_2H_6 is 15 : 1. No dissolved CO was detected in the experiment. This might be attributed to the shift of the water-gas shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$) to the right side due to the loss of H_2 at high temperature and pressure conditions [19, 20], resulting in conversion of CO to CO_2.

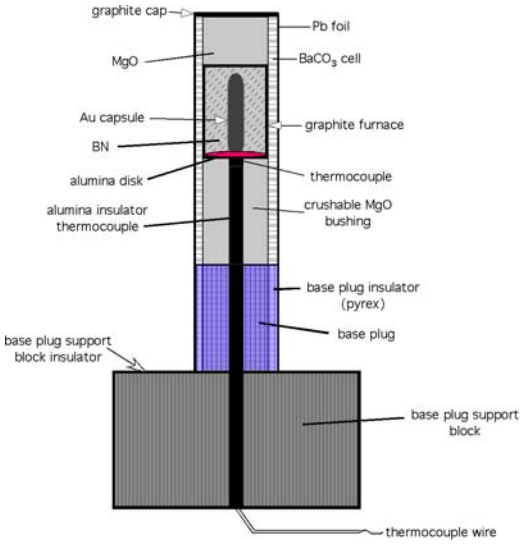

Figure 1. Schematic diagram showing piston cylinder assembly used for hydrothermal experiments.

Carbon isotopes. The $\delta^{13}C$ value of formic acid used in the experiment was -22.4‰ (V-PDB). CO_2 derived from decarboxylation of formic acid had the $\delta^{13}C$ value of -19.2‰, which was 3.2‰ heavier than its source. For alkanes, the $\delta^{13}C$ values of CH_4 and C_2H_6 were -50.3‰ and -39.3‰, respectively.

The pattern of $\delta^{13}C$ values between CO_2 and CH_4 is consistent with their equilibrium pattern ($CO_2 > CH_4$). The magnitude of this fractionation (31.1‰), however, is much higher than the corresponding value of 9.4‰ based on theoretical isotopic equilibrium predictions at 750 °C [21]. For alkanes, CH_4 is 11‰ less enriched in ^{13}C than C_2H_6. The $\delta^{13}C$ difference between CH_4 and C_2H_6 is higher than the equilibrium fractionation value of ~ 0.6 at 750 °C [22].

Discussion: The suggested criterion for distinguishing alkanes of abiogenic origin from thermogenic origin is the "inverse correlation" of $\delta^{13}C$ and $\delta^{2}H$ values for *n*-alkanes: $\delta^{13}C$ value decreases and $\delta^{2}H$ increases with increasing molecular mass [13-15]. Previous studies have shown that experiments designed to produce hydrocarbons via abiogenic reactions do not consistently produce ''inverse trends'', and that organic derived gases can also display similar isotopic patterns analogous to the abiotically formed hydrocarbons [11, 16, 17, 23]. Results of these studies suggest that reaction mechanism/pathway, which in turn is controlled by physical and chemical conditions (mineral catalyst, redox, T, P, etc.), could be the crucial factor affecting fractionation of carbon and hydrogen isotopes.

In this study (750 °C and 0.55 GPa) the $\delta^{13}C$ difference between CO_2 and CH_4 is 31.1‰. This is higher than the values (4.6 to 27.1‰) observed in similar experiments performed at 400 °C and 50 MPa with longer reaction times [16]. Combined with ^{13}C mass balance calculation which indicates the existence of other carbon-bearing compounds either on mineral surfaces or in solution, it suggests that the reaction pathway/organic intermediate(s) might be different under different T and P conditions. The $\delta^{13}C$ values of C1 and C2 alkanes in this experiment, however, increased with carbon number, which is the same as the carbon isotope pattern observed in lower T and P conditions [16].

As suggested by Fu et al. (2007) [16], the reaction pathway of hydrothermal FTT synthesis involves formation of long chain hydrocarbons on mineral surfaces, followed by depolymerization and/or reaction with other hydrocarbons. A set of experiments at different physical and chemical conditions with different reaction time, which are in progress, are needed to confirm above hypothesis, and elucidate the reaction pathway and its controlling factors of hydrothermal abiotic organic synthesis.

Conclusions: An experiment involving hydrothermal abiotic organic synthesis was conducted using a piston cylinder apparatus at 750 °C and 0.55 GPa. CH_4 and C_2H_6 were observed in fluid products. The $\delta^{13}C$ value of CH_4 is 11‰ less than that of C_2H_6. No carbon isotope reversal trend was observed for alkanes with increasing carbon number.

Considering the importance of mineral catalyzed organic synthesis as a likely source of hydrocarbons in hydrothermal fluids and the potential effect of this on microbial metabolism on the seafloor and other planets, it is necessary to understand more completely the wide range of chemical and physical factors that can contribute to formation of organic compounds. Assessing carbon and hydrogen isotope patterns associated with hydrocarbons, could be instrumental in constraining the origin and evolution of organic species on the seafloor and other planets.

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